Thermodynamics of the bilinear-biquadratic spin one Heisenberg chain

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The magnetic susceptibility and specific heat of the one-dimensional $S = 1$ bilinear-biquadratic Heisenberg model are calculated using the transfer matrix renormalization group. By comparing the results with the experimental data of LiVGe$_2$O$_6$ measured by Millet et al. (Phys. Rev. Lett. **83**, 4176 (1999)), we find that the susceptibility data of this material, after subtracting the impurity contribution, can be quantitatively explained with this model. The biquadratic exchange interaction in this material is found to be ferromagnetic, i.e. with a positive coupling constant.

The quantum spin chains have been the subject of many theoretical and experimental studied since the conjecture made by Haldane [1] that the antiferromagnetic Heisenberg model has a finite excitation gap for integer spins. The model which has been intensively used to investigate the physics behind the Haldane's conjecture is the isotropic spin one Heisenberg Hamiltonian with both bilinear and biquadratic spin interactions:

$$H = J \sum_i \left[\mathbf{S}_i \cdot \mathbf{S}_{i+1} + \gamma (\mathbf{S}_i \cdot \mathbf{S}_{i+1})^2 \right]. \tag{1}$$

For most of the existing quasi-one-dimensional (1D) $S = 1$ materials, the biquadratic term is very small compared with the bilinear term as well as the uniaxial anisotropy. This model was therefore generally thought to be of pure theoretical interest. However, recently Millet et al. [2] found that the magnetic susceptibility of a new quasi-1D $S = 1$ system, the vanadium oxide LiVGe$_2$O$_6$, shows a few interesting features which are absent in other $S = 1$ materials. They argued that both the interchain coupling and the uniaxial anisotropy are too small to create these features and suggested that the biquadratic term plays an important role in this material.

In this paper, we present a theoretical study for the thermodynamics of the bilinear-biquadratic spin chain (1) with $J > 0$. We have calculated the magnetic susceptibility and specific heat of this model using the transfer matrix renormalization group (TMRG) method [3–6]. By comparing with the experimental data of LiVGe$_2$O$_6$, we find that the measured susceptibility, after subtracting the impurity contribution, can be quantitatively fitted by the numerical result with $\gamma = 1/6$. This shows that the spin dynamics of LiVGe$_2$O$_6$ can indeed be described by the Hamiltonian (1), in agreement with Millet et al. [2]. However, the value of γ needed for fitting the experimental data is different from that suggested by Millet et al. [2].

Let us first consider the properties of the ground state. It is known that when $\gamma = -1$ and 1, the model (1) can be solved rigorously by the Bethe Ansatz [7,8]. Between these two soluble points, the system is in the Haldane phase. In this phase, the ground state is a non-magnetic singlet with a finite energy gap in excitations. In particular, when γ is between -1 and $\gamma_{ic} \approx 0.41$, the low energy physics of this model can be understood from the valence bond solid (VBS) model proposed by Affleck *et al.* [9]. In this model, each site on the chain is occupied by two $S = 1/2$ spins and the ground state is formed by the bonding of two $S = 1/2$ spins from adjacent sites. These singlet bonds must be broken in order to excite the system and this leads to a non-zero energy gap in the low-lying spectrum. This picture has been confirmed experimentally [10,11] as well as numerically [12]. At γ_{ic}, the ground state undergoes a commensurate-incommensurate transition and the critical exponent for the magnetization changes from $1/2$ below γ_{ic} to $1/4$ above γ_{ic} [13,14]. Between γ_{ic} and 1, the system is in the incommensurate phase and the incommensurate peak in the spin form factor $S(q)$ of the ground state moves continuously from π to $2\pi/3$ as γ increases from γ_{ic} to 1 [15,16]. Above $\gamma = 1$, the true nature of the ground state is still controversial [15–17]. Some works [15,16] suggest that it might be in a trimerized phase. When $\gamma < -1$, the ground state is doubly degenerate and dimerized.

The TMRG is a finite temperature extension of the powerful density matrix renormalization group method [18]. A detailed introduction to this method can be found in references [3–6]. The TMRG method handles directly infinite spin chains and thus there is no finite system size effects. To calculate the spin susceptibility, we first evaluate the magnetization M of the system with a small external field B, and then from the ratio M/B we obtain the value of the susceptibility. The specific heat is evaluated from the numerical derivative of the internal energy with respect to temperature. At low temperatures, since the specific heat is very small, the relative error of the specific heat may become quite large. In most of our calculations 100 states are retained.

Figure 1 shows the zero-field spin susceptibility $\chi(T)$ normalized by the its peak value χ_{peak} as a function of the normalized temperature T/T^s_{peak} for a set of γ, where T^s_{peak} is the temperature of χ_{peak}. Above T^s_{peak}, $\chi(T)/\chi_{\text{peak}}$ behaves similarly for all the curves shown in the figure. When γ is positive, $\chi(T)$ drops quickly below

T^s_{peak}. This is because the energy gap in this parameter regime is very large. As γ becomes negative, $\chi(T)$ just below T^s_{peak} tends to become flatter. At $\gamma = -1$, there is no gap in the excitation spectrum, $\chi(T)$ shows a small positive curvature at low temperatures, as in the $S = 1/2$ Heisenberg chain.
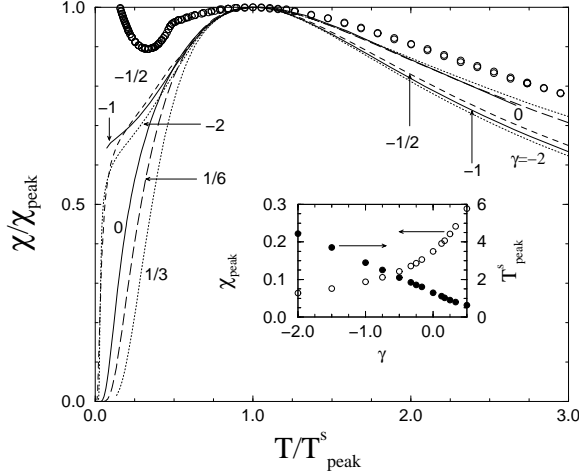

FIG. 1. The normalized spin susceptibility χ/χ_{peak} as a function of T/T_{peak} at zero field. The experimental data of LiVGe$_2$O$_6$ obtained by Millet et al [2] (empty circles) are also shown for comparison. The inset shows the γ dependence of the peak susceptibility χ_{peak} (empty circles) and the peak temperature T^s_{peak} (filled circles). J is set to unit.

The inset of Figure 1 shows the γ dependence of χ_{peak} and T^s_{peak}. The increase of χ_{peak} with γ indicates that the susceptibility becomes larger when γ moves from the dimerized phase to the Haldane phase. This is consistent with the picture that in the dimerized phase the spin is frozen by forming rather rigid spin singlet, while in the Haldane phase the spin is relatively free above the Haldane gap. The peak temperature T^s_{peak} drops almost linearly with γ. The slope of this drop is about $1.6J$ per unit γ.

In a gaped phase, the low-lying excitation has approximately the energy dispersion

$$\varepsilon_k = \Delta + \frac{v^2}{2\Delta}(k - k_0)^2 + O\left((k - k_0)^3\right), \qquad (2)$$

where k_0 is the wavevector of the excitation minimum, Δ is the energy gap and v the spin velocity. When $T \ll \Delta$, it can be shown that $\chi(T)$ has the form [19]

$$\chi(T) \approx \lambda\sqrt{\frac{\Delta}{T}}e^{-\Delta/T}, \qquad (3)$$

where λ is a T-independent parameter. From the fit of the low temperature TMRG results of $\chi(T)$ with this equation, we can estimate the value of Δ. The result of Δ we obtained is shown in Figure 2. The maximum energy gap is $\sim 2J/3$, located at $\gamma = 1/3$. Our results agree with other numerical studies [17,20].
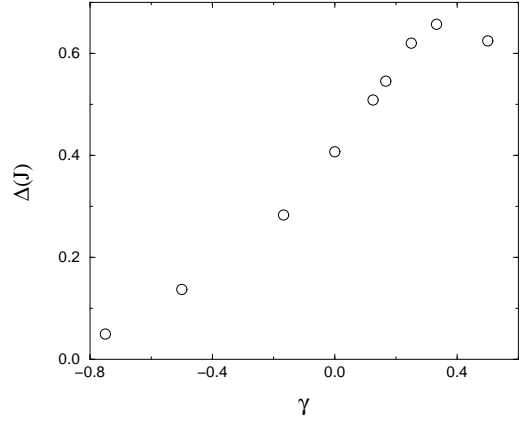

FIG. 2. The energy gap as a function of γ.

Figure 3 shows the temperature dependence of the specific heat $C(T)$ for a set of γ. The inset of the figure shows the γ dependence of the peak value of the specific heat, C_{peak}, and the peak temperature T^c_{peak}. Compared with T^s_{peak}, T^c_{peak} behaves quite differently. It drops with increasing γ when $\gamma < 1/2$ and becomes almost a constant when $\gamma > 1/2$. Below the peak temperature, C/C_{peak} shows quite similar behavior for all the curves shown in the figure except at very low temperatures. Since there is no energy gap at $\gamma = \pm 1$, $C(T)$ at these two points approaches to zero linearly with decreasing T. However, for other cases, $C(T)$ decays exponentially at low temperatures. For the two exact solvable point $\gamma = \pm 1$, exact results are available [21], the specific heat vanishes linearly at low temperature. However, due to large errors at low temperatures, our results do not show this behavior clearly. Above the peak temperature, C/C_{peak} drops quickly for negative γ. However, when γ becomes bigger, in particular in the incommensurate phase ($\gamma = 2/3$ and 1), $C(T)$ shows a weak and broadened peak above T^c_{peak}. It seems that there is a new excitation mode accumulated at low energies in the incommensurate state.

Now let us compare the numerical results with the spin susceptibility data χ_{exp} of LiVGe$_2$O$_6$ measured by Millet et al. on a powder sample [2]. As mentioned in [2], two extraordinary features appear in χ_{exp}. One is the slow drop of χ_{exp} on both sides of the susceptibility peak, and the other is the abrupt drop of χ_{exp} below $22K$ with a sharp upturn below $15K$. The first feature, in particular the slow drop of χ_{exp} below the peak temperature, is reminiscent of a gapless system. The second feature of χ_{exp} is typical of a spin-Peierls system with impurities, such as in Zn doped CuGeO$_3$ [22]. These features have led Millet et al. to interpret LiVGe$_2$O$_6$ as a nearly gapless $S = 1$ spin chain with the spin-Peierls instability. However, whether the abrupt drop of χ_{exp} at $22K$ is really due to a spin-Peierls transition is still an open question.
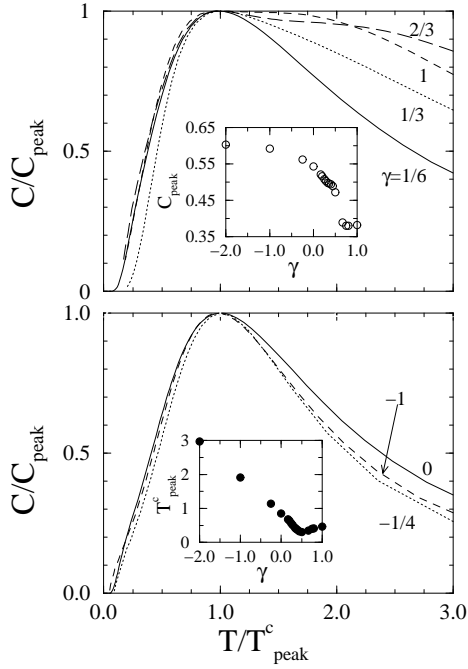
FIG. 3. The normalized specific heat C/C_{peak} as a function of T/T_{peak}^c. The upper and lower panels are for γ larger and smaller than zero, respectively. The upper inset shows the peak specific heat C_{peak} and the lower one shows the corresponding temperature T_{peak}^c. J is set to unit.

The sharp upturn of χ_{exp} at low temperatures indicates that the impurity contribution is strong. To see how strong the impurity effect is, let us first do a comparison without subtracting the impurity contribution in χ_{exp}. In Figure 1, the measured susceptibility χ_{exp} normalized by its peak value at about $47K$ is compared with the TMRG results discussed previously. The disagreement between the theoretical and experimental results indicates that the impurity effect is too strong to be ignored even at high temperatures.

The susceptibility of dilute magnetic impurities generally has a Curie-Weiss form

$$\chi_{\text{imp}} = \frac{C'}{T + \theta' + \alpha T^{-1}}, \qquad (4)$$

where C' is proportional to the impurity concentration and the square of the effective g-factor of the impurity and θ' is a measure for the interaction among impurities. The αT^{-1} term in χ_{imp} is the leading order correction to the Curie-Wess term $C'/(T + \theta')$ due to the finite magnetic field. If there is no interaction between impurities, $\alpha = (2S'^2 + 2S' + 1)(g'\mu_B B/k_B)^2/10$ with g' and S' the effective g-factor and spin of impurities. This term is not important at high temperatures. But when the temperature becomes comparable with the level splitting of an impurity spin in a magnetic field, this term becomes important. It prevents χ_{imp} from being divergent at low temperatures. α is typically of order $1K^2$ when $B = 1T$.

At very low temperatures the measured susceptibility

is a sum of χ_{imp} and $\chi(T)$ given by Eq. (3), i.e.

$$\chi_{\text{exp}}(T) = \chi_{\text{imp}} + \lambda\sqrt{\frac{\Delta}{T}}e^{-\Delta/T}. \qquad (5)$$

By fitting the low temperature experimental data below $15K$ with this equation, we find that $C' = 0.115cm^3K/mol$, $\theta' = 14.1K$, $\alpha = 2.18K^2$, $\lambda = 0.0063cm^3/mol$ and $\Delta = 36K$. These parameters show that not only the contribution from impurities to χ_{exp} is large as expected, but also the interaction among impurities is strong at low temperatures. There is no simple explanation for such a strong correlation among impurities. Clearly this is an important problem which should be further investigated both theoretically and experimentally.
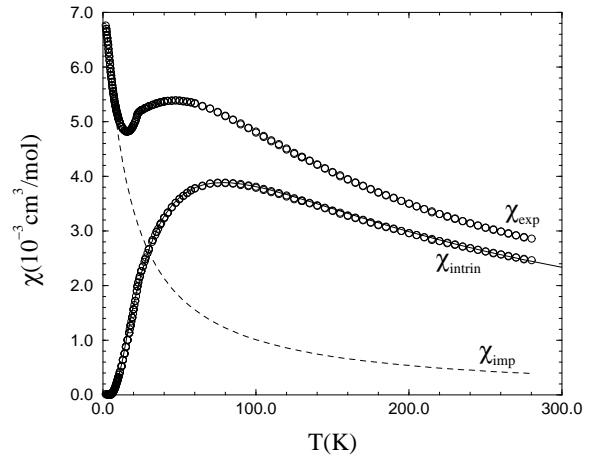

FIG. 4. Comparison of the TMRG result (solid line) of the spin susceptibility of the $S = 1$ bilinear-biquadratic model with $J = 73K$ and $\gamma = 1/6$ with the experimental data of LiVGe$_2$O$_6$ [2]. χ_{intrin} is the experimental data after subtracting the impurity contribution χ_{imp} from χ_{exp}.

By subtracting the impurity contribution from χ_{exp}, we obtain the intrinsic susceptibility χ_{intrin} of LiVGe$_2$O$_6$. The result of χ_{intrin} together with the raw data χ_{exp} and χ_{imp} is shown in Figure 4. After the subtraction, the abrupt drop of χ_{exp} at $22K$ becomes less distinct, but the change in the slope is still visible. The most significant change of χ_{intrin} compared with χ_{exp} is that the peak shifts to a higher temperature and the drop below the peak temperature becomes more rapidly. By comparing in detail the normalized χ_{intrin} with the theoretical results, we find that χ_{intrin} can be well fitted by the numerical curve with $\gamma = 1/6$ (Figure 4). This shows that the biquadratic term in model (1) does have an important contribution to the low energy spin dynamics of LiVGe$_2$O$_6$, in agreement with Millet et al. [2]. However, the value of γ which gives the best fit, in particular its sign, is different from that suggested in Ref. [2]. A detailed comparison indicates that χ_{intrin} lies between the theoretical curves for $\gamma = 1/4$ and $1/8$ in the whole tem-

perature region. Thus the uncertainty in the value of γ_c is very small. The result at $\gamma_c \sim -1$ suggested in Ref. [2] does not fit the experiment data.

At $\gamma = 1/6$, the peak temperature is $T^s_{\text{peak}} = 1.025J$. Setting this T^s_{peak} equal to the peak temperature of χ_{intrin}, we find that $J \sim 73K$. Compared with the gap value $\Delta = 36K$ obtained previously, we have $\Delta \sim 0.49J$. This value of Δ is rather close to the Haldane gap, $0.54J$, of the Hamiltonian (1) at $\gamma = 1/6$ (Figure 2). This suggests that the low energy spin excitations are gapped and the change of the slope at 22K is not due to a spin-Peierls transition.

We have also compared χ_{intrin} with the spin susceptibility of the $S = 1$ Heisenberg model with uniaxial single-ion anisotropy but without the biquadratic term [23], namely the model $H = J \sum_i \left[\mathbf{S}_i \cdot \mathbf{S}_{i+1} + D \sum_i S^2_{iz} \right]$. However, in the parameter region which might be physically relevant, $-1/2 < D < 1/2$, we find that none of the numerical curves fits χ_{intrin} in the whole temperature range. This shows that the uniaxial anisotropy in LiVGe$_2$O$_6$ is indeed very small, in agreement with the analysis of Millet et al. [2].

The above analysis confirms the importance of the biquadratic exchange interaction in LiVGe$_2$O$_6$. On the other hand, it also raises some new questions. In the argument given by Millet et al., the biquadratic term comes from in fourth order since at second order the antiferromagnetic and ferromagnetic terms partially cancel. However, the coefficient of this biquadratic term is negative (i.e. $\gamma < 0$) according to their calculation, in contrast with the result we obtain. To resolve this disagreement, further investigation into the electronic structure of LiVGe$_2$O$_6$ is needed. More detailed measurements with high quality single crystals would also help clarify the impurity effect as well as the nature of the anomaly at $22K$ in this material. In a $S = 1$ Heisenberg chain, the localized non-magnetic impurity may induce mid-gap states within the Haldane gap [24–27]. A better understanding of the physical properties of these mid-gap states would also be helpful for further understanding the thermodynamics of LiVGe$_2$O$_6$ at low temperatures.

In summary, the thermodynamic properties of the bilinear and biquadratic Heisenberg model have been studied and compared with the experiments. The measured susceptibility data of LiVGe$_2$O$_6$, after subtracting the impurity contribution, can be quantitatively explained by the model (1) with $\gamma = 1/6$.

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